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PART I

THERMAL DEGRADATION OF POLYESTERS

I. ALIPHATIC POLYMERS

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task 734203, "Fundamental Principals Determining the Behavior of Macromolecules." It was administered under the direction of the Air Force Materials Laboratory with Dr. I. J. Goldfarb as Task Scientist.

This report covers work conducted from 1 January 1967 to 1 April 1968.

The authors wish to thank Mr. R. R. Luthman, Jr., for his valuable assistance in the experimental work and in the calculations. Thanks are also due to Dr. H. Friedman and Dr. H. Goldstein, General Electric Space Sciences Laboratory, for the Mass Spectral Thermal Analyses and to the Monsanto Research Corporation for the Gas Chromatography/Mass Spectrometry.

This technical report has been reviewed and is approved.

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ABSTRACT

A study has been made of the pyrolysis of eight aliphatic polyesters prepared from various diacids and diols. The polymers start to degrade at about 275°C by random scission of the ester linkage and are comparable to poly(ethylene terephthalate) with respect to thermal stability. Providing a β-hydrogen atom is available in the diol portion of the ester, which was the case for the polymers studied, the classical cyclic mechanism observed for the decomposition of simple esters is applicable. Differences in degradation behavior are best explained in terms of secondary reactions which are dependent upon the nature of the end-groups formed by scission and on the chain length of the acid and diol used to prepare the polymer. Thus, olefinic end-groups break down to aldehydes, dienes, cyclic ethers, and enols while acid end-groups give carbon dioxide, cyclic ketones (C_5-C_7 diacids), and cyclic anhydrides (C_4, C_5 diacids). Water is produced by anhydride formation and dehydration of hydroxyl end-groups.

The overall kinetics were consistent with a random mechanism but deviations from the simple random picture were concluded for some polymers and probably resulted from cross linking. Kinetic parameters were evaluated from programmed TGA data; activation energies of approximately 40 kcal/mole and preexponential factors of about 10^{12} min^{-1} were obtained.

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SECTION I

INTRODUCTION

Because of the predominant use of the condensation type of polymers for high-temperature applications and the continuous search for thermally stable structures, there is a growing need to systematically study the thermal degradation of condensation polymers. To this end, this research has been devoted to a detailed study of polyesters and this first part of the report is concerned with aliphatic polymers which, owing to their ease of dissolution, purification, and characterization, are amenable to systematic study.

The specific objectives of the study were to establish the major reaction mechanisms in aliphatic systems, to examine the kinetics of degradation, and to observe the effects of varying the acid or glycol parts of the polymer on the thermal stability and reaction mechanisms.

Two series of polymers were investigated. For the first, the acid part (sebacic acid) was common and the glycol part varied; for the second, the reverse situation was effected using octamethylene glycol and succinic, glutaric, adipic, and pimelic acids. These can be represented by the structures,

$$\left[O \left(CH_2 \right)_x \overset{O}{\overset{\|}{C}}O \text{ } \left(CH_2 \right)_y \overset{O}{\overset{\|}{C}} \right]_n$$

Sebacates $x = 2, 3, 4, 5;\ y = 8$

Octamethylene polymers $x = 8;\ y = 2, 3, 4, 5$

Kinetic studies of the degradation of the above polyesters were made by temperature-programmed thermogravimetry. Comparison of stabilities by this method was supplemented by isothermal studies. Information concerning the reaction mechanisms involved in the degradation was obtained by product analysis. Infrared spectroscopy and combined gas chromatography-mass spectrometry were among the techniques employed for this purpose. The polymers were also studied by time-of-flight mass spectrometry, which in theory can yield both kinetic and analytical information, but which in this study was used mainly as an analytical tool.

SECTION II

REVIEW OF PREVIOUS WORK ON ESTER PYROLYSIS

Very little has been published on the degradation of aliphatic polyesters. The original work by Carothers (Reference 1) on polyesters is sometimes quoted as the standard reference for aliphatic polyester pyrolysis. It should be noted, however, that Carothers was interested in synthesizing macrocyclic structures for synthetic perfume bases and used catalysts to obtain cyclic lactones from polyesters.

Most ideas about the reaction mechanisms are inferred from analogy to simple esters and poly(ethylene terephthalate) which, because of its great commercial importance, has been studied in detail. The gas-phase pyrolysis of simple esters has been extensively investigated. An elimination reaction forming acid and olefin usually prevails when a β-hydrogen atom is available in the alcohol part of the ester. A cyclic transition stage is generally accepted and very consistent kinetics have been observed for a wide range of esters (References 2 through 5). A study of di-(2-ethyl-hexyl) sebacate, a good model for the polymers being presently studied, showed that the liquid phase decomposition followed first-order kinetics with an activation energy of 47 kcal mole^{-1} and preexponential factor of 10^{12} sec^{-1} (Reference 6). This compared very well with the E_a values of about 45 kcal mole^{-1} found for the gas-phase decomposition of simple esters.

For poly(ethylene terephthalate), the pyrolysis is much more complex; reactions competing with the elimination described above and secondary reactions of the products of primary scissions have to be considered (References 7 through 10). A random thermal cleavage of ester groups is observed but small amounts of water can provide an alternative hydrolytic path. Secondary reactions, e.g., decarboxylation, decarbonylation, and anhydride formation, are observed. Vinyl ester groups formed by primary scission breakdown to give acetaldehyde in copious quantities. In Ritchie's paper (Reference 9), a brief mention of saturated aliphatic polymers and models is made and it was concluded that the the size of the acid part did not noticeably affect the stability of the ester linkage.

Two recent studies of aliphatic polyesters have appeared in the literature, a thermo-oxidative study of poly(ethylene adipate) and poly(ethylene sebacate) (Reference 11) and a nonoxidative degradation study of several adipate polyesters (Reference 12). This latter work is particularly relevent and comparable to the present research. Olefin, carbon dioxide, and cyclopentanone were the important degradation products. The kinetics were found to be first order with $E_a = 44 \pm 2$ kcal mole^{-1}. It was concluded that the stability of the polyester increased with increasing chain length of both acid and glycol parts of the ester.

SECTION III

EXPERIMENTAL

POLYMERS

All but one of the polyesters were prepared under contract AF-33(657)-10819 by Wyandotte Chemicals Corporation. The polymers were white, powdery solids and had properties listed in Table I. The polymers were reprecipitated from benzene solution before use; this caused an increase in the number average molecular weight, which is shown in the table. The tetramethylene sebacate polymer was prepared in this laboratory by Dr. M. Tessler, using trans-esterification techniques (Reference 13). A small excess of glycol is normally used in such polymerizations so that the end-groups are usually hydroxyl groups rather than carboxylic acid groups.

M. W. MEASUREMENT

Number average molecular weights (M_n) were measured using a Mechrolab vapor-phase osmometer, model 302 (Hewlett-Packard Co.). Benzene was the solvent. The experimental technique employed has been described by Goldfarb and Meeks (Reference 14).

TABLE I

PROPERTIES OF POLYESTERS

Polymer	Symbol	M. P. (° C)	Elemental Analysis (%)				Number Average M. W.	
			Theoretical		Observed			
			C	H	C	H	Original	Reprecipitated
Octamethylene Succinate	O1	62	63.13	8.83	63.16	8.77	4,600	6,450
Octamethylene Glutarate	O2	53	64.43	9.15	64.29	8.98	4,575	9,150
Octamethylene Adipate	O3	63	65.60	9.44	65.50	9.44	3,380	6,100
Octamethylene Pimelate	O4	55	66.64	9.69	66.46	9.62	3,350	8,100
Ethylene Sebacate	S1	76	63.13	8.83	63.01	8.82	4,800	12,300
Trimethylene Sebacate	S2	49	64.43	9.15	64.41	9.13	5,680	12,100
Pentamethylene Sebacate	S3	52	66.64	9.69	66.41	9.60	5,270	8,800
Tetramethylene Sebacate	S4	59	65.60	9.44	65.75	9.42	2,000	3,300

TGA WEIGHT LOSS STUDIES

The apparatus used for temperature-programmed TGA studies has been previously described (Reference 15). The thermobalance was the commercially available "Ainsworth Thermobalance." Samples weighing 50 to 100 mg were degraded under high-vacuum conditions by raising the temperature from 25° to 500°C at a controlled, approximately constant heating rate. Weight and temperature were continuously recorded. Each polymer was subjected to at least four heating rates in the range 1.3 to 7.5C°/minute. The method used to obtain kinetic parameters from this TGA data has been fully discussed in another report (Reference 16) and is essentially that described by Friedman (Reference 17) and reviewed with other methods by Flynn and Wall (Reference 18). Calculations were done on an IBM 7094 computer. The computer programs are fully described in Reference 16.

ISOTHERMAL STUDIES

Polymer samples, 100 to 200 mg, were pyrolyzed isothermally on a conventional, manifold type of vacuum line. Pyrolysis was stopped after a predetermined time and the weights of residue, condensate, and volatiles were determined. Product analysis was performed on the separated fractions.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

Volatile product fractions, i.e., those products collected in a liquid nitrogen trap, were submitted for GC/MS analysis. The analyses were done by Monsanto Research Corporation under AFML (Analytical Branch) contract No. F33615-67-C-1363. Components were separated and identified using an F&M 700 gas chromatograph. Typical separating conditions consisted of a 12-ft 20% Triton X-305, 60/80 mesh Gas Chromium Z column, 275°C flame ionization detector, helium carrier gas (80 psi., 50 ml/min) and programmed temperature (50° to 170°C, 8°C/min). Quantitative calculations were then made from a composite mass spectrum obtained from a CEC 21-100L rapid-scan mass spectrometer.

TIME OF FLIGHT MASS SPECTROMETRY

The polyesters were submitted for mass spectrometric thermal analysis (MTA) to Dr. H. Friedman and Dr. H. Goldstein of General Electric Company (USAF Contract No. F33615-67-C-1372). Drs. Friedman and Goldstein have made

a full description of the apparatus and technique in References 19 and 20. In the general MTA procedure, individual masses, M/e = 1-210, are continuously scanned as the temperature is programmed from 25° to 900°C, so that individual intensity-temperature profiles are obtained for each mass. In theory, both kinetic and quantitative product analyses can be obtained. Since the full possibilities of MTA are still being developed, a qualitative approach was adopted with respect to the polyesters. To simplify qualitative analysis and to allow the data for different polymers to be easily compared, MTA results were reduced to conventional bar graphs by plotting the maximum intensities of product peaks against M/e.

IR SPECTROSCOPY

A Perkin-Elmer Model 521 spectrophotometer was used. Samples were examined as pressed KBr films (solids) and films between salt plates (liquids).

SECTION IV

RESULTS

TGA RATES AND KINETICS

Since the treatment of TGA data to obtain kinetic parameters has been fully discussed in Reference 16, a less detailed description is given here.

From the weight, temperature, and time data obtained from the experimental thermograms, rates of weight loss and temperatures were calculated by computer for constant conversion increments, 1%, 2% . . . 99%. For aliphatic polyesters, no residue is formed so that, in deriving rates and conversions, percent sample weight and percent weight loss are equivalent, eliminating any confusion over choice of units. The calculations were repeated for each heating rate (B). To illustrate the effect of heating rate, a typical set of derivative rate (DTG) curves is shown in Figure 1. It is interesting to compare these DTG curves for the series of polymers as is done in Figure 2, in which, for clarity, only one heating rate is represented. The same observations are made for any heating rate. Several of the rate curves in Figure 2 are very similar both in position and shape. It must also be realized that the heating rate is only approximately constant, ranging from 2.45 to 2.70°/minute. The apparent higher stability of S1 and the broader, low maximum curves of S1 and S2 stand out as differences beyond any experimental error or heating rate change.

Rate-conversion curves are less useful for comparison among polymers and a typical curve is shown in Figure 3. It was observed that most of the polymers gave curves which were slightly concave initially. The conversion corresponding to the maximum rate was difficult to locate precisely since the results tended to be somewhat scattered over the broad maximum. Thus, rate maximums were observed between 50 and 70% conversions although most curves had the maximum in a smaller range, 55 to 60%. As will be discussed later, rate-conversion curves are of considerable diagnostic value, as are the corresponding curves in isothermal treatments (Reference 21).

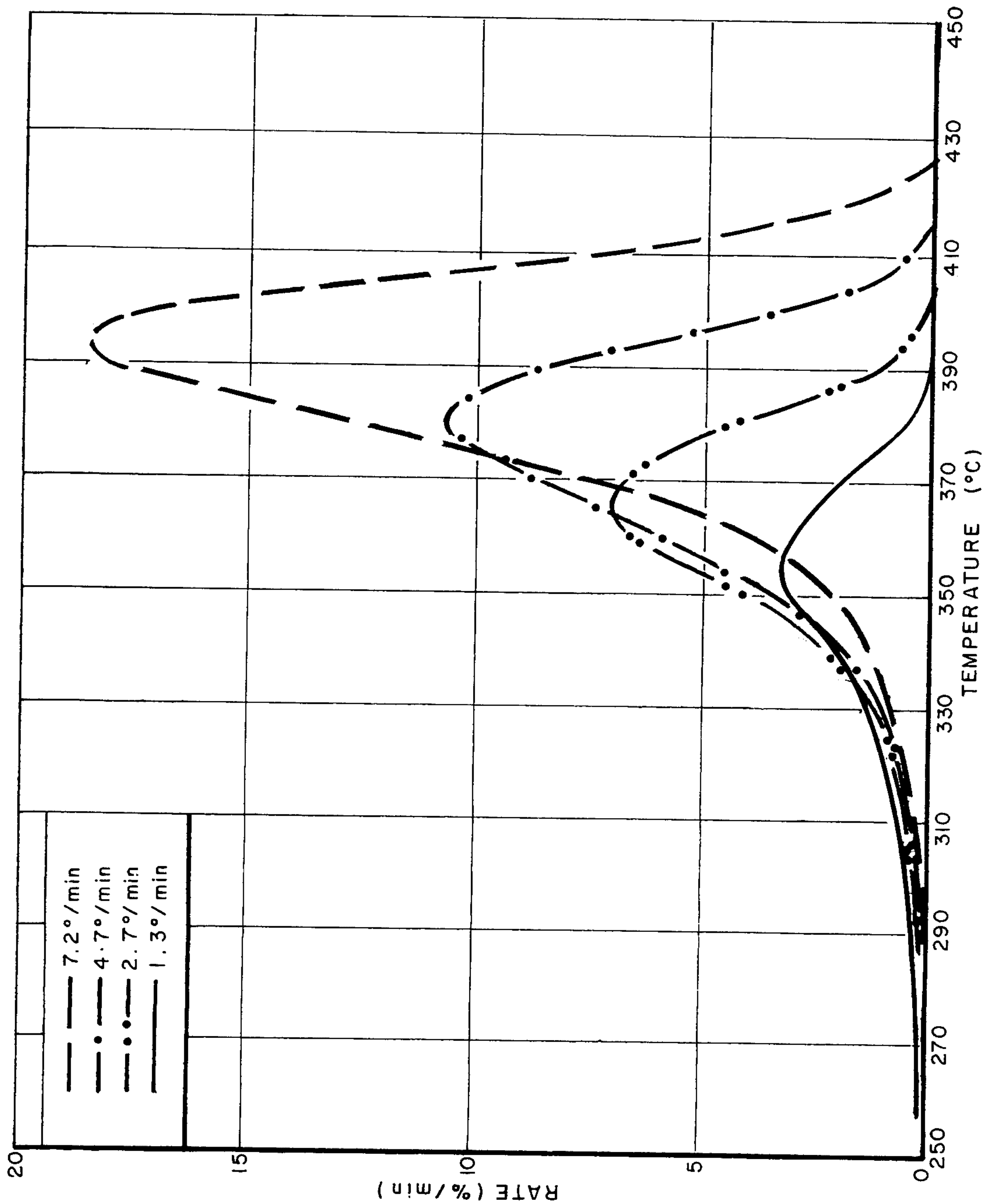


Figure 1. DTG Rate Curves for Polymer O1 at Several Heating Rates

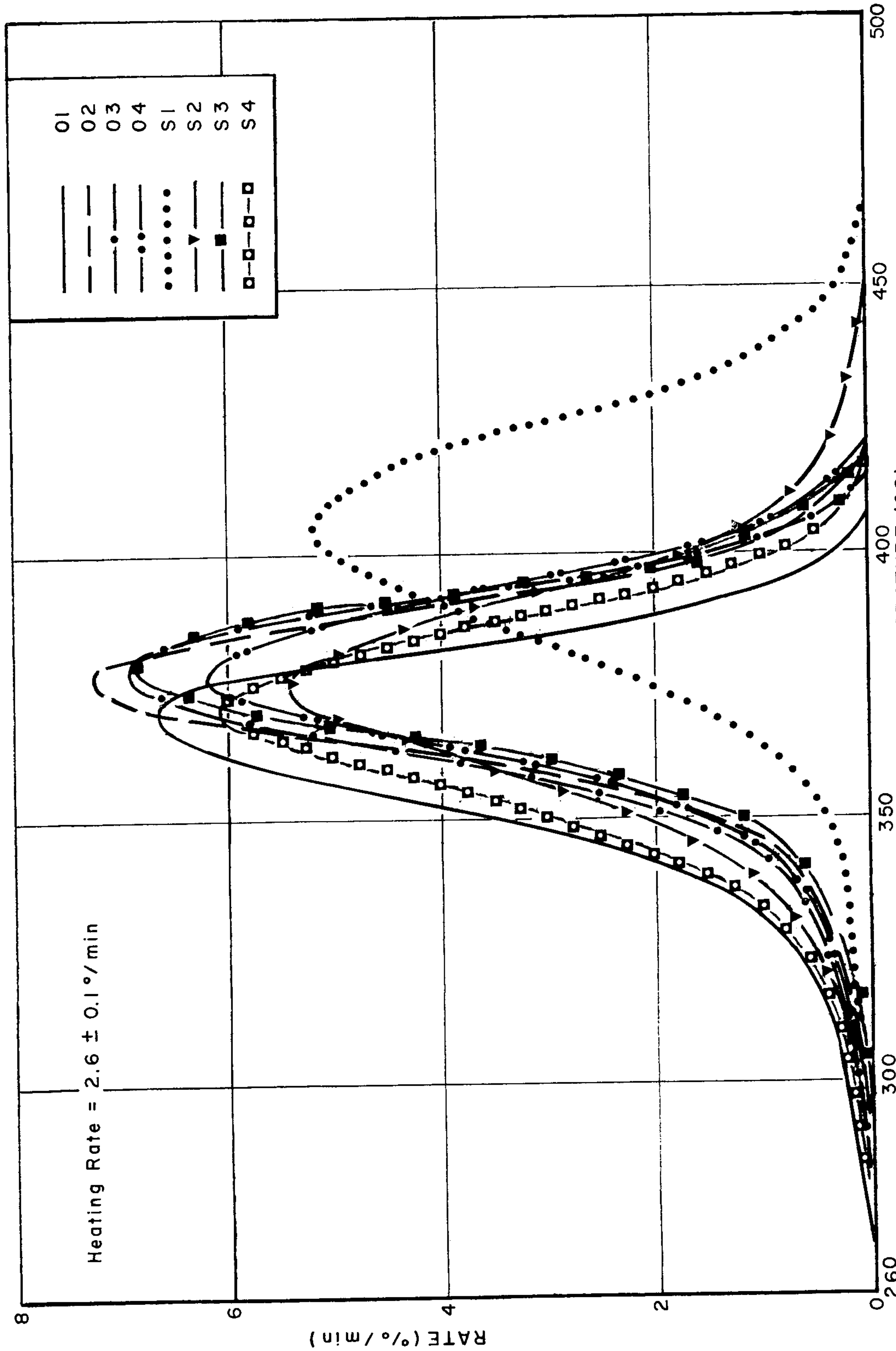


Figure 2. Comparative DTG Curves for Polyesters at One Heating Rate

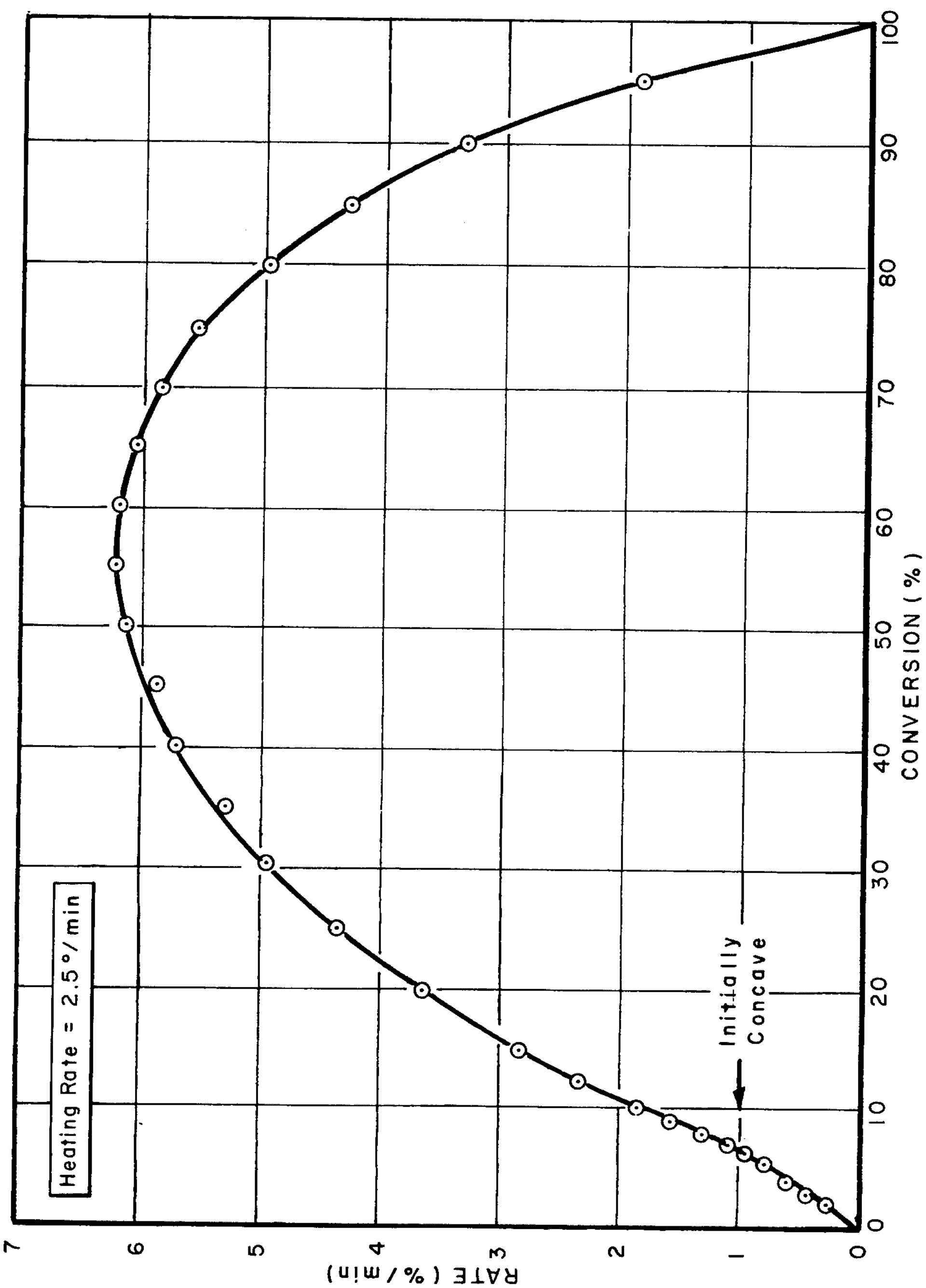


Figure 3. Rate-Conversion Curve for Polymer O4 at One Heating Rate

Activation energies (E_a) were computed as a function of conversion from the rate-temperature data discussed above. The basic Arrhenius type of equations used for the calculations are given below:

$$\text{rate} = \left(-\frac{1}{W_0}\,\frac{dW}{dt}\right)_B = A\,\exp\left(-\frac{E_a}{RT_B}\right)\cdot F(W) \qquad (1)$$

$$\log\,(\text{rate})_B = -\frac{E_a}{2.303R}\left(\frac{1}{T_B}\right) + \log\left[A\;\;F(W)\right] \qquad (2)$$

In these equations, dw/dt is the rate of weight loss, W_o is the total weight lost in the degradation or sample weight in these polyester samples, F(W) is a non-defined function of weight, T is temperature, A the prexponential factor, E_a the activation energy, and R the gas constant. The suffix, B, indicates that the rate and temperature are dependent upon the heating rate employed. At each conversion, it is assumed that log $\left[A\;\;F(W)\right]$ is a constant, independent of heating rate, B, so that, when the rate-temperature data corresponding to various heating rates are plotted according to Equation 2, a straight line results, from which E_a is easily calculated. Calculated activation energies are shown in Figures 4 and 5 as a function of conversion. Except for the initial and final stages of the degradations, the activation energy was approximately constant and an average value for the conversion range, 10 to 80%, was calculated. The fit of the data in each individual E_a calculation was examined by computing the standard deviation of the fitted least-squares line (Table II).

To establish the functionality of W from Equation 1, i.e., the rate law governing the kinetics, average E_a values were used in Equation 2 to compute log $\left[A\;\;F(W)\right]$ as a function of conversion. Results were plotted as shown in Figure 6 and salient kinetic features summarized in Table II. The significance of these results is discussed later.

PRODUCT ANALYSIS

In both isothermal and programmed studies, the total weight loss was composed of condensate and volatile fractions; condensates remained in the degradation column immediately above the hot zone, and "volatiles" were trapped in a liquid nitrogen trap. Table III gives approximate distributions of the fractions, which are limited by errors involved in retrieving small amounts of

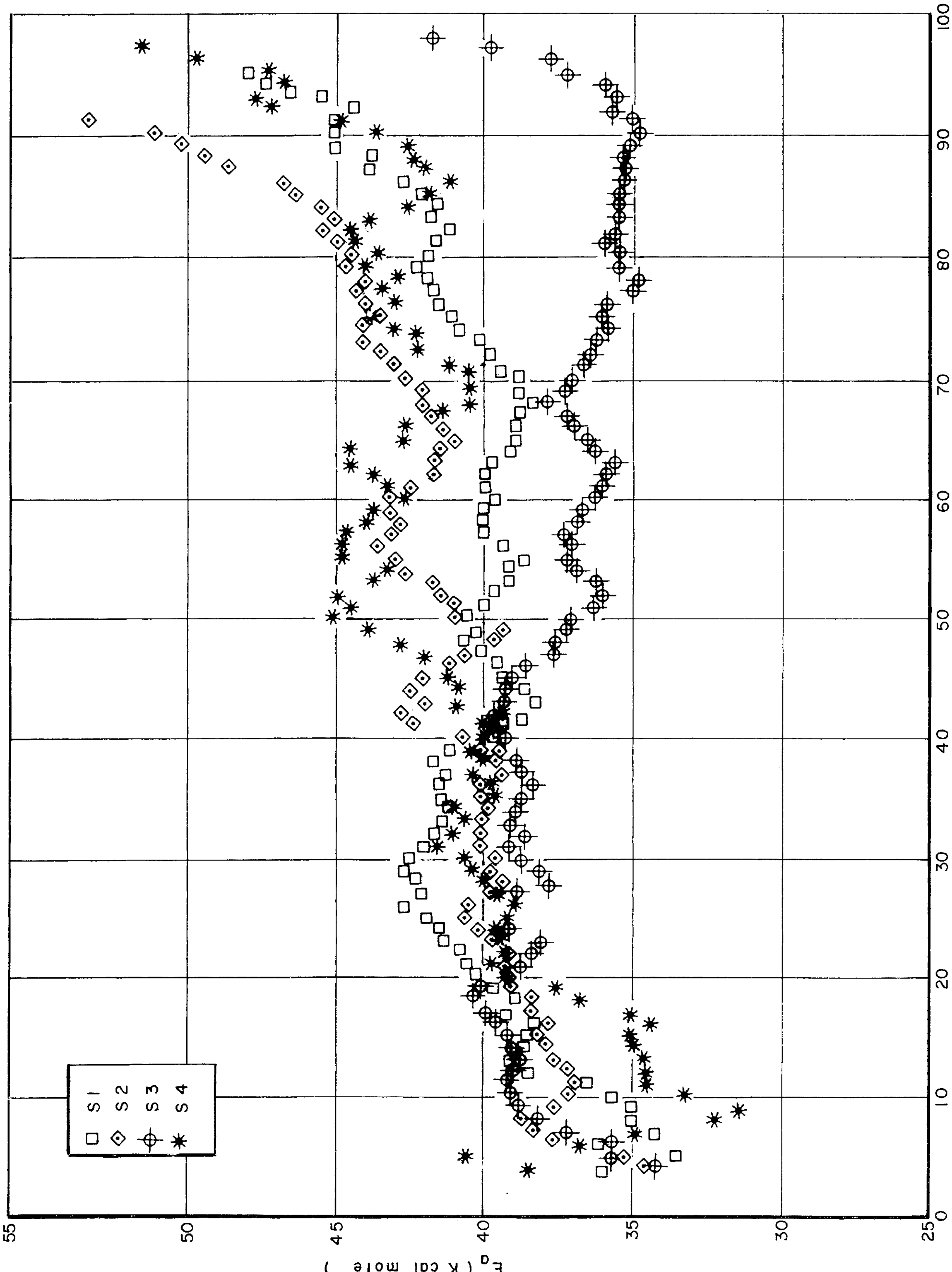


Figure 4. Activation Energy Vs Conversion Relationships for S Polymers

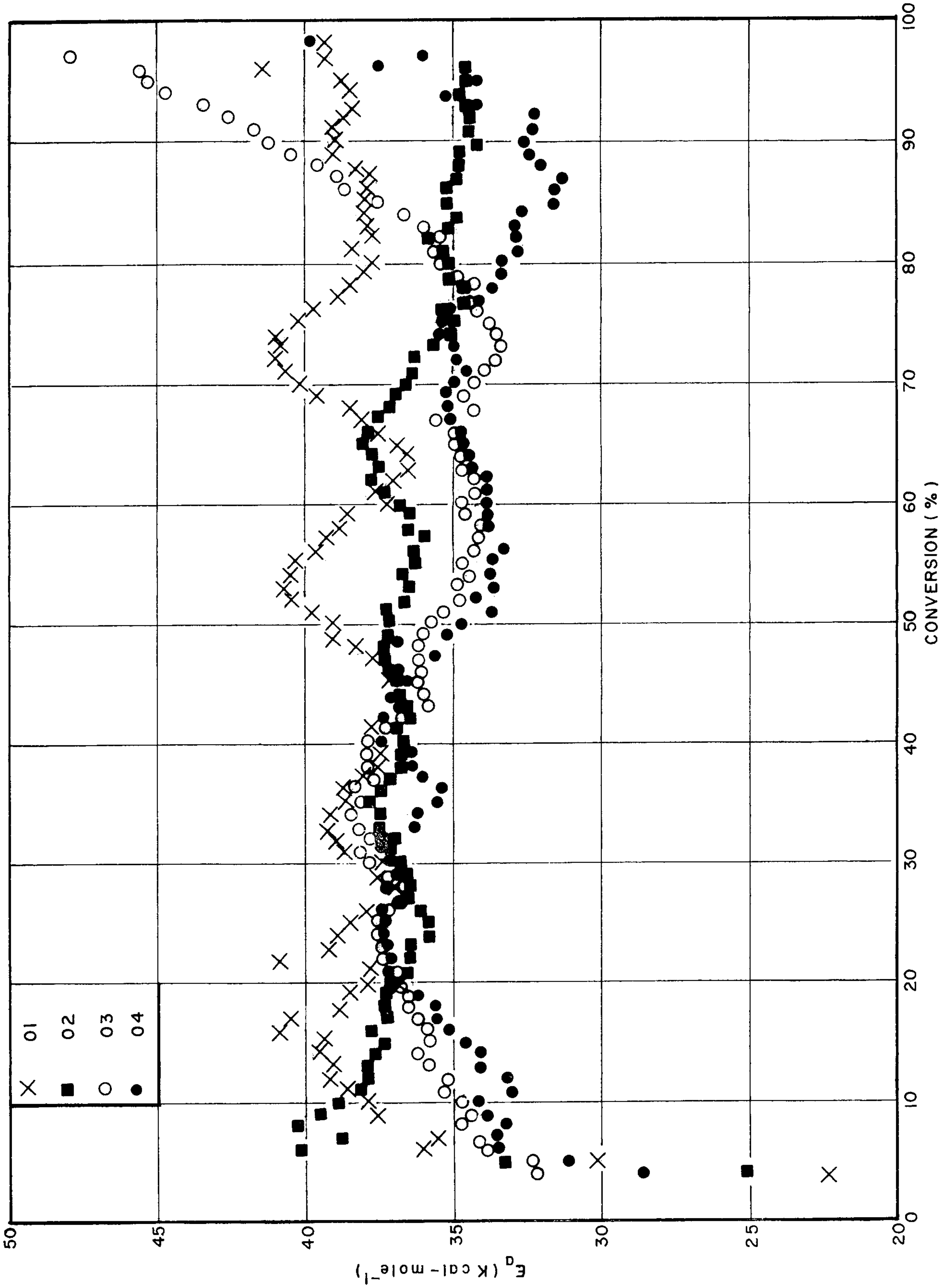


Figure 5. Activation Energy Vs Conversion Relationships for O Polymers

TABLE II

OBSERVED KINETIC PARAMETERS

Polymer	Ea (10-80%) (kcal mole^{-1})	Average Standard Deviation of Ea (kcal mole^{-1})	Log $\left[A\ F(W)\right]$ at Maximum (% min^{-1})	Conversion at Maximum (%)
S1	40.2	1.6	13.83	18 and 23
S2	41.1	1.5	14.71	23 and 26
S3	37.9	2.4	13.64	26
S4	40.9	3.0	14.76	25
O1	38.6	2.5	14.07	26
O2	36.8	3.9	13.35	29
O3	35.8	4.8	13.02	24
O4	35.4	4.0	12.81	27

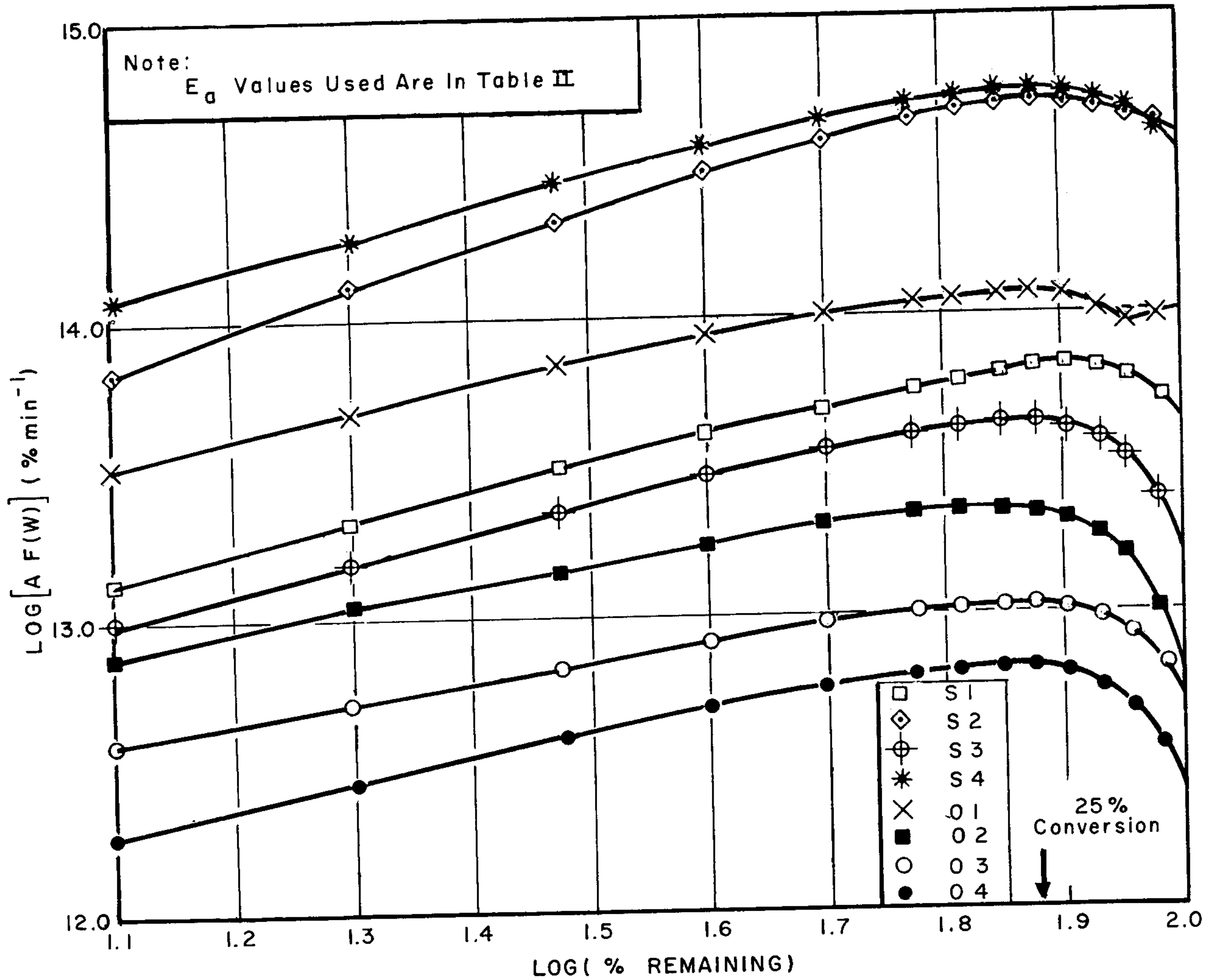


Figure 6. Rate-Law Plots, Log $\left[A\ F(W)\right]$, for Polyesters

TABLE III

PERCENTAGE CONDENSATE FRACTION* OF TOTAL WEIGHT LOSS

	% Condensate Fraction	
	Programmed TGA	Isothermal Wt. Loss
S1	53	58
S2	68	80
S3	87	76, 87
S4	Not measured	
O1	72	76
O2	72	77, 77
O3	93	89, 77
O4	83	89, 85

*Remainder corresponds to volatile fraction.

material from a bulky glass system. Volatile fractions were derived by difference rather than by direct weighing. In the TGA of aliphatic polyesters, no residues were obtained since complete volatilization of the sample took place during the main degradation step (270° to 450°C). To study residues, isothermal reactions were not carried to complete degradation but were stopped at a point which would provide residues amounting to 60 to 85% of the starting polymer weight (Table IV).

Residues

The residues obtained ranged from waxy materials to tough, hard rubbers. They were yellow to light brown in color, except for polymers S2 and O1 which were dark brown in color. The IR spectra of residues from isothermal degradations at 300°C showed no visible changes from the original polymer. The IR spectra obtained from experiments at 342°C showed some slight changes, as listed in Table V with some other observations.

TABLE IV

ISOTHERMAL WEIGHT LOSS RESULTS

	Percent Weight Loss	
	360 min at 300° C	60 min at 342° C
S1	-	15.2
S2	19.2	20.6
S3	12.5	25.8
O1	27.0	40.0
O2	19.7	31.4
O3	11.9*	24.2
O4	15.9	25.8

*Time was reduced to 200 min instead of 360 min.

The tendency for polymers to become insoluble in benzene under the mildest of degradation conditions prevented detailed M.W. studies to be made. The few measurements which were made suggested that the M.W. tended to decrease gradually with conversion and no dramatic fall in M.W. was observed. Suspected gellation, however, made these observations unreliable.

Condensates

The condensates from programmed runs consisted of a yellow to brown oil near the top of the furnace, and for some polymers, S2, S3, O3, and O4, a clear wax could be discerned above the oil. The wax fraction was 10 to 30% of the total condensate. The oils were soluble in benzene and carbon tetrachloride, the waxes somewhat soluble in these solvents and soluble in methanol. Conclusions drawn from IR spectral investigations are given in Table VI. The oils were identified as low M.W. oligomers, a fact confirmed by VPO; the molecular weights formed from the oils from O1 and O3 polymers were 745 and 836 respectively. These molecular weights correspond to approximately 3.5 repeat units. The waxy materials were of lower molecular weights, as concluded from

TABLE V

PROPERTIES OF DEGRADATION RESIDUES FROM ISOTHERMAL STUDIES AT 342° C

Polymer	Appearance	Solubility in Benzene	IR Spectrum
S1	Light color, tough, rubbery	Insoluble, gels	Almost identical to original, trace anhydride, COOH, C=C.
S2	Brown, tough, rubbery	Insoluble, gels	COOH and C=C showing
S3	Light color, soft, waxy	Partly soluble	Spectrum similar to original but small amounts of anhydride COOH and C=C showing
O1	Dark brown, tough rubber	Insoluble	As original with C=C showing (1640 cm^{-1})
O2	Fawn color, soft, waxy	Partly soluble	As original with C=C evident
O3	Fawn color, soft, waxy	Partly soluble	Trace amounts of COOH C=C and anhydride showing
O4	Fawn color, soft, waxy	Partly soluble	Trace anhydride and unsaturation

TABLE VI

TGA CONDENSATES

Polymer	Lower Condensate	Upper Condensate
S1	THF fractions: mainly ester some COOH, C=C groups. MeOH fraction: mainly ester with OH and new absorptions at 1600, 1640, 1660 cm^{-1}. Small amounts of β-diketone or similar structure may be present.	None
S2	Ester with some COOH groups.	No end-groups observed. Possibly cyclic "dimer."
S3	Ester with some COOH groups and olefinic groups.	Mixture of acid-ester and sebacic acid.
O1	Ester plus $\alpha - \beta$ unsaturated ester.	None
O2	Ester with olefinic groups, trace COOH.	Similar to lower condensate.
O3	Ester with CO_2H and olefinic groups.	Similar to lower condensate. Stronger COOH and C=C groups.
O4	Ester with CO_2H, C=C, and possible conjugated C=C (1610 cm^{-1}).	Same as lower condensate.

the much stronger end-group intensities in the IR and probably consisted of one or two repeat units. In one case, O3, the dibasic acid itself was suspected.

Isothermal condensates could also be divided into two fractions, a colorless oil near the hot zone and a smaller weight of white wax above the oil. In this case, however, as shown in Table VII, the upper condensates could be much better defined. These observations applied to both the 300° and 342°C degradations. Generally speaking, the upper condensate was the dibasic acid and in the cases where it was not observed, it was found that the acid part had carried over to the trap in the form of the anhydride (polymers O1 and O2). The lower condensates were similar to the starting polymers except that small amounts of

TABLE VII

ISOTHERMAL DEGRADATION CONDENSATES

Polymer	Lower Condensate	Upper Condensate
S1	Ester group dominates but C=O absorption complex, possibly COOH, anhydride.	Strong acid absorption competing with ester group.
S2	Ester with strong acid and anhydride absorptions.	Sebacic Acid
S3	Ester with acid, anhydride, and olefinic groups.	Sebacic Acid
S4	Ester-acid.	Sebacic Acid
O1	Ester with hydroxyl and olefinic groups.	Very small amount of crystalline 1, 8-octanediol (1).
O2	Ester with CO_2H, C=C and possible OH groups.	None (2)
O3	Ester with CO_2H, C=C groups.	Adipic Acid
O4	Ester with CO_2H, anhydride, and olefinic groups.	Pimelic Acid

Notes: (1) Succinic acid was found in "volatile" trap after volatiles had been transferred. Succinic anhydride also found in several experiments.

(2) Glutaric anhydride was found in "volatile" trap.

other groups, presumably end-groups, were now seen. It was not a simple matter to identify those small groups since the intense ester group and sometimes the acid carboxyl group tended to mask small peaks developing in that region. The formation of ketones could be easily missed in the IR for this reason.

Color Formation

In an attempt to determine the structure(s) responsible for the development of yellow to brown coloration in the residues and condensates, several condensates were examined in the UV and visible ranges. In most samples examined, no

changes could be detected, but one condensate fraction which was very dark in color, showed new absorptions in the form of a doublet with maxima at 427 and 455 mu. A literature search revealed only one structure which would give such an absorption and would also be compatible with possible ester reactions; this was the α -diketone grouping which was concluded to form in small amounts during degradation.

Volatile Products

The results of GC/MS analysis are given in Tables VIII and IX; MTA data in the form of bar graphs are given in Figures 7 and 8. Quantitative analysis of the MTA results was prevented by lack of calibration data for the complex mixture of products. A comparison of the MTA data can be used to check the reliability of the GC/MS data.

In Figure 7, differences resulting from the changing glycol part of the polymers are readily observed. In the S1 spectrum, the strongest peaks are M/e = 15, 29, and 44 corresponding to acetaldehyde. In the spectra of S2 and S3, the strong CO_2 peak dominates the spectrum. In S3, however, the peaks corresponding to the diene and, to a lesser extent, the enol or isomer, derived from the glycol part of the ester, become important. For S4, the corresponding peaks of butadiene (M/e = 56) and tetrahydrofuran (M/e = 72) are both strong, suggesting a much higher THF content than observed by GC/MS; the respective base peaks of M/e = 39 and 42 are the strongest in the spectrum. The water peak at M/e = 18 is more important than it appears, since water has a low base-peak sensitivity. A comparison of the ratios of the 18-to-44 peaks for the various polymers suggests that the low water content observed for S1 in the GC/MS analysis is erroneous. The relative amount of water as measured by the H_2O/CO_2 ratio was highest for the lowest M.W. polymer (S4) and lowest for the highest M.W. polymers, S1 and S2. The remaining S and O polymers gave intermediate values but no conclusive correlations were made. Clearly, a study of M.W. fractions of a single polymer would be more satisfactory for attempting to relate water formation with the starting concentration of hydroxyl end-groups. MTA also suggests a significant amount of carbon monoxide (M/e = 28) which is not observed in the GC/MS since the trapping techniques used in preparing the samples allow CO to pass through. Without detailed quantitative analysis, the

TABLE VIII

MOLE PERCENT PRODUCT DISTRIBUTIONS
OF S POLYMERS BY GC/MS ANALYSIS

	S1	S2	S3	S4
Carbon dioxide	38.7	25.5	14.6	28.2
Water	3.2	26.9	21.9	20.2
Acetylene	-	1.0	-	-
Ethene	3.2	0.8	0.7	6.0
Propene	1.4	13.4	2.2	5.8
Butene	0.7	0.2	1.8	3.1
Pentene	0.4	3.3	-	1.0
C_6 olefin	0.2	2.1	1.5	0.3
C_7 olefin	-	0.6	2.9	-
Acetic acid	0.5	0.4	-	-
Acetone	0.7	-	-	-
Cyclohexane	-	-	1.8	-
Cyclohexene	-	2.1	-	-
Cyclohexadiene	-	0.3	-	-
Butadiene	0.2	0.4	0.4	31.9
1, 4 Pentadiene	0.7	-	4.4	-
Acetaldehyde	50.1	1.4	1.2	-
Allyl alcohol	-	6.7	-	-
Propanaldehyde	-	13.4	-	-
Butanaldehyde	-	1.4	-	-
1, 3 Pentadiene	-	-	29.1	1.0
4-Pentene-1-ol	-	-	17.5	-
Tetrahydrofuran	-	-	-	2.5

TABLE IX

MOLE PERCENT PRODUCT DISTRIBUTIONS
OF O POLYMERS BY GC/MS ANALYSIS

	O1	O2	O3	O4
Carbon Dioxide	17.3	17.6	14.7	32.4
Water	33.3	38.1	16.9	23.5
Cyclohexene	9.8	32.3	20.3	32.1
Butadiene	2.7	-	0.4	0.6
Acetone*	18.0	1.9	9.0	-
Ethene	3.0	3.9	5.6	-
Propene	2.0	0.5	3.4	0.2
Butene	2.6	0.1	0.4	0.5
C_5 olefin	2.7	0.4	-	0.6
C_5 diolefin	-			0.5
C_6 olefin	1.2	0.1	-	0.4
C_7 olefin	0.2	0.6		0.1
C_7 diolefin	-	-	0.7	-
C_8 olefin	0.5	2.3	-	-
C_8 diolefin	1.9	-	0.4	0.6
Acrolein	3.8	-	-	-
Cyclobutanone	-	1.6	-	-
Cyclopentanone	-	-	28.2	-
Cyclohexanone	-	-	-	8.4

* Probably an impurity

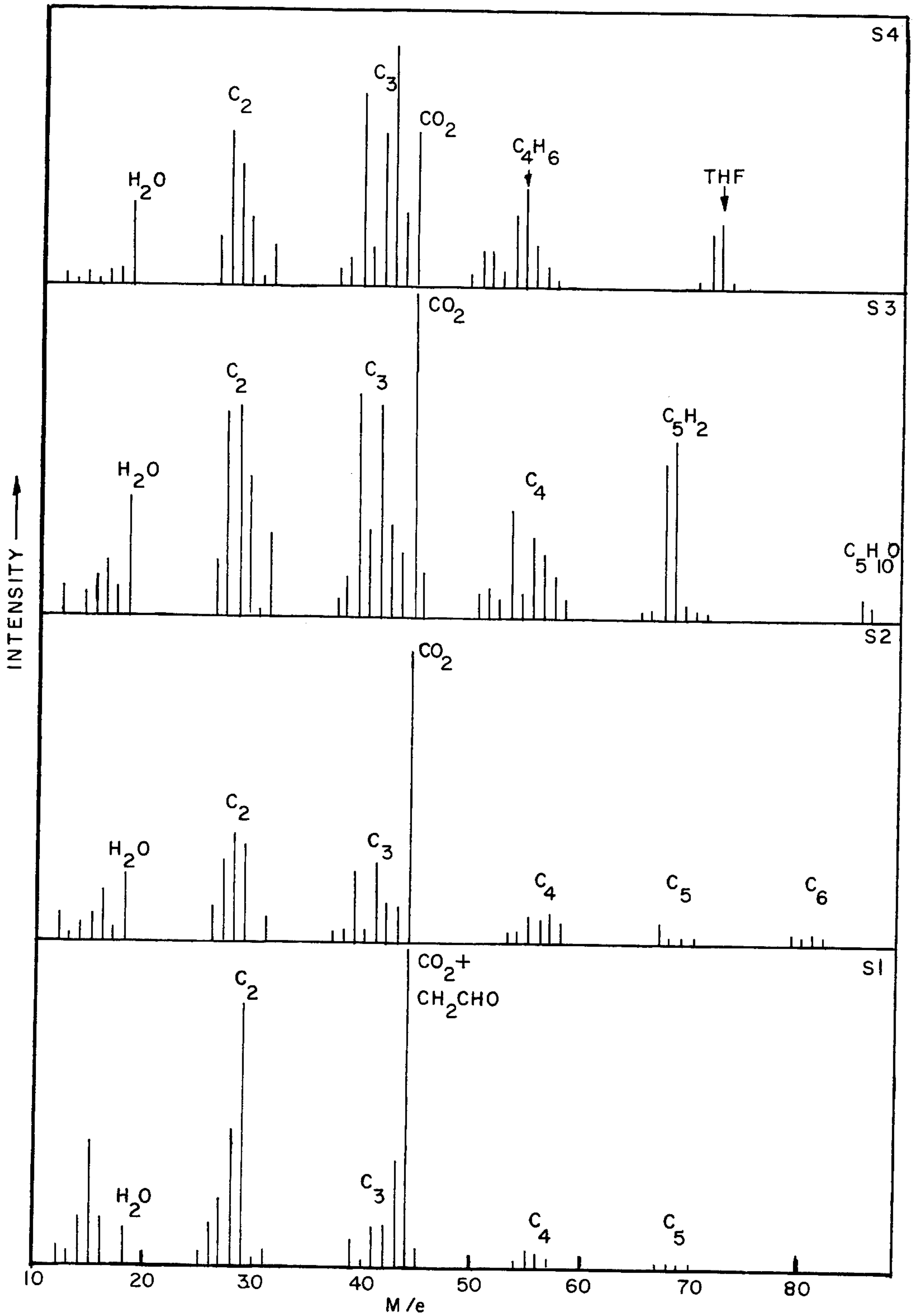


Figure 7. Important Peaks in MTA Spectra for S Polymers

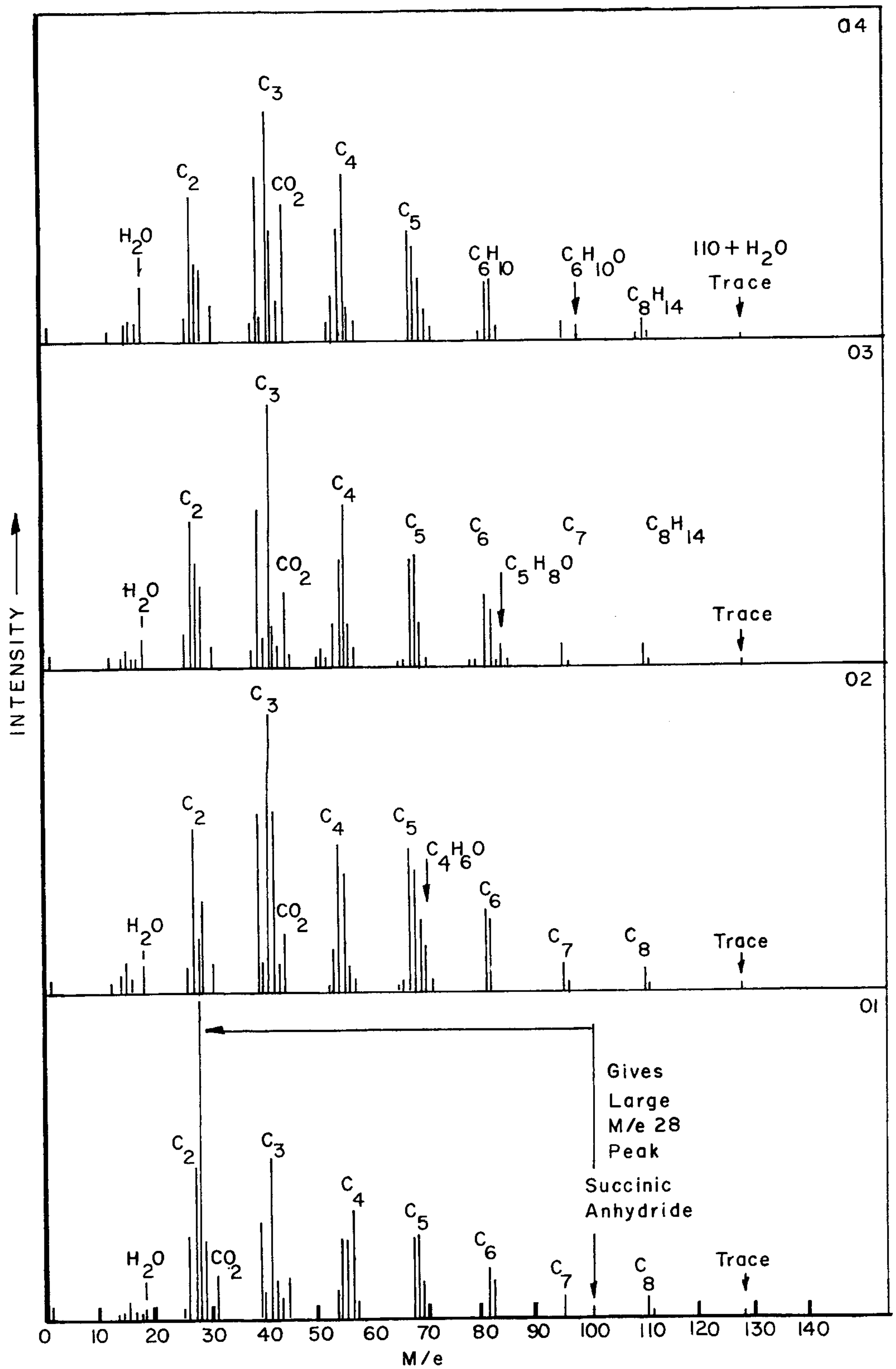


Figure 8. Important Peaks in MTA Spectra for O Polymers

actual amount of carbon monoxide is difficult to establish since ethylene and fragments from higher M.W. products contribute to the M/e = 28 peak.

In Figure 8, MTA of the O polymers can be compared with Table IX. In the MTA spectra, the fragmentation derived from the C_8 part of the ester dominates and causes much similarity in the spectra. Except for O1, the polymers have the strongest peak at M/e = 41. The anomalous peak, M/e = 28, in O1 is caused by the succinic anhydride for which 28 is the base peak. Compared to the spectra for the S polymers, the H_2O and CO_2 peaks are much smaller.

Judging from the MTA spectra, the GC/MS technique has failed to analyze the C_8 and related products properly. It is possible that these higher products were not seen in the GC and contributions from these in the MS were wrongly assigned. Thus, high values of cyclohexene are observed in the GC/MS table. Peaks corresponding to a C_8 diolefin in the MTA are quite significant, but in the GC/MS table, the C_8 diolefin is scarcely detected. The highest product observed was a very small peak at 128. (Some higher ones in the 133 and 205 regions can be attributed to silicon grease components and mercury respectively.) This finding corresponds to an octenol or isomeric species, and the product thus identified could be important since the parent peaks of alcohols are generally very small. The structure of these higher compounds is uncertain since, as has been observed in the S polymers, rearrangements, double-bond shifts, and cyclization can take place in the splitting out of the linear glycol fragment. Since numerous peaks occurred from the C_8 part of the O polymers, differences deriving from the acid part are less noticeable. In O1 succinic anhydride (M/e = 100) and acrolein (M/e = 56) are diagnostic. In O2, O3, and O4 peaks corresponding to cyclobutanone (M/e = 70), cyclopentanone (M/e = 84), and cyclohexanone (M/e = 98) are observed.

The above discussion of volatile products by MTA concurs with the observations made by Friedman on the MTA of polyesters (Reference 22). The data presented represents the main degradation process occurring at about 400°C in the MTA. Specifically, the peaks correspond to the maximum evolution of products. Several other features were discerned by MTA; some polymers, especially S1 and S3, showed some early evolution giving a small mass peak or

tail before the main degradation peak. The ability to observe this depends on the intensity of the major peak which, if strong, may mask small initial peaks. For S1, peaks could be observed at M/e = 18, 31, 45, 60, and 78, but no assignations were attempted. Traces of solvents and impurities could be seen at lower temperatures, 100° to 200°C. A curious feature of the MTA peaks was the tendency for long tails to show in the temperature range 500° to 900°C. This was ignored in the present analysis since TGA showed more than 99% weight loss at 500°C for all the aliphatic polymers.

SECTION V

DISCUSSION

KINETICS OF DEGRADATION

One of the objectives of this study was to obtain precise values of kinetic parameters which would allow comparisons between closely similar polymers. It is clear from the scattering of results that this aim has still to be achieved. The results for some polymers were less gratifying than others and, in retrospect, reasons for this became obvious. It was found, e.g., that polymer S4 tended to splutter, especially at high heating rates, causing the thermograms to be "noisy" and subject to irregularities. If loss occurs because of spluttering, higher rates of weight loss are observed at higher heating rates, so that the observed activation energy is higher than it should be. The reason for scattered results in polymers O2, O3, and O4 was that smaller samples (50 mg) were degraded at chart speeds which were too slow. As a result steep thermograms were produced which were more difficult to reduce to accurate weight-time data. The experimental arrangement used is also subject to a serious procedural error. In this method, the accurate measurement of temperature is of critical importance since the shift in temperature caused by varying the heating rate is relatively small. Thus, e.g., a change in heating rate from 1.3°/min to 7.5°/min gave a temperature range of about 35° to 40°C for the occurrence of a given weight loss. For the apparatus used, calibrations were performed to relate the actual polymer temperature to that of the recording thermocouple which was not in contact with the sample. As suspected, a heating lag existed which increased with heating rate and varied during the degradation. In the present study, approximate corrections were made based on heating rate alone and the results given for activation energies are some 5 kcal mole^{-1} higher than would have been obtained if corrections had not been made. Since corrections were not made as a function of conversion, or more appropriately, as a function of rate, further errors may result. This may be responsible for the slump in the E_a-conversion curves of some of the polymers, e.g., S3, S4, O2, and O4. The true activation energy may be a little higher, therefore, than was generally observed. In future work, we hope to measure polymer temperature directly to obviate errors of this nature.

The overall rate loss can be discussed in terms of Figures 3 and 6. Flynn and Wall have examined hypothetical examples and discussed the differences caused by varying kinetic parameters in the resulting TGA curves (Reference 18). Thus, the curve presented in Figure 3 is consistent with a random mechanism; the fact that the maximum rate occurs at 55 to 60% conversion does not distinguish between a random mechanism and a pseudo first-order scheme but the two mechanisms are resolved by the initial part of the curve where concavity is a strong indication of a random degradation. The log $\left[A\ F(W)\right]$ plots in Figure 6 lend stronger support to this conclusion. In the temperature-programmed method, this plot is somewhat analogous to the rate-conversion curve in isothermal studies. In such studies, ''random'' rate curves are well known (Reference 23) and are distinguished by a maximum at 26% conversion. This is equivalent to what occurs in Figure 6, although the maximums tend to be somewhat scattered. It should be realized that any error in E_a used to compute log $\left[A\ F(W)\right]$ is reflected not only in the value of log $\left[A\ F(W)\right]_{max}$ but also in its location. In the classical equations developed for random degradation (References 23 and 24), the functionality of W is complex:

$$F(W) = (L-1)\,W/W_0 - (1-\alpha)^L\,(N-L)\,(L-1)/N \tag{3}$$

in which L = critical chain length for evaporation,

N-1 = initial chain length, and

α = fraction of bonds broken.

This complex function is not linear with respect to weight so that plots against weight functions as in Figure 6 are not linear. If F(W) could be assigned a theoretical value, the experimental data could be tested in a similar log-log plot. This can be done using the empirical function used by Flynn and Wall (Reference 18).

$$F(W) = N\,(c^3 + a_1 c^2 + a_2 c + a_3) \tag{4}$$

where N is a normalizing factor, C is the conversion $(1 - \frac{W}{W_0})$, and a_1, a_2, and a_3 can be calculated for various boundary conditions. Experimental data was tested against functions of this type and linear log-log plots obtained. It was noted that the slopes for such plots were approximately unity for the O samples but usually higher than one for the S samples. This agrees with Figure 6 in

which it is shown that the S polymers especially S2 give steeper slopes toward higher conversions than do the O polymers. This effect is probably caused by representing the degradation by an average E_a when in some polymers there was a distinct upward trend in E_a throughout the degradation. If the upward trend is real, the use of an average E_a would skew the log A F(W) plot in the direction observed. It is usual in kinetic evaluations to determine the preexponential factor A (Equation 1) corresponding to the activation energy observed. The complexity of F(W) in the random case makes this extremely difficult since is unknown, being itself a function of the various Arrhenius parameters for bond scission.

$$\alpha = 1 - \exp\left[-A\left(\exp\frac{-E_a}{RT}\right)\cdot t\right] \qquad (T\ \text{constant}) \qquad (5)$$

$$\alpha = 1 - \exp\left[-\frac{A}{B}\int_{T_0}^{T}\exp\left(-\frac{E_a}{RT}\right)\cdot dt\right] \qquad (T\ \text{programmed}) \qquad (6)$$

This problem is usually circumvented by using an approximation developed in Reference 23 for the maximum rate. In the present treatment, the equivalent equation would be:

$$\log\left[A\ \ F(W)\right]_{max} = \log A + \log L/e \qquad (7)$$

The validity of this approximation is suspect unless the rigid boundary conditions for Simha and Wall's derivations are adhered to. The important condition is that the initial chain length should be very much greater than the chain length which evaporates (L in Equation 3). This condition is not met, since the initial M.W. for those condensation polymers is low. Note, however, that the log L/e term in Equation 6 is very small compared to the log A term. Thus, log $\left[A\ F(W)\right]_{max}$ can be used as an approximate log A value. The observed values (Table II) of log $\left[A\ \ F(W)\right]$ give A values, 10^{11} to 10^{13} min^{-1}, where the units have been changed from weight percent to weight fraction.

A further important consequence of the complexity of F(W) is that temperature has not been completely accounted for and there is doubt as to whether F(W) is really constant for constant conversions (W/W_0) and whether it is also independent of heating rate. By developing Equation 6 it can be shown that is constant for a given weight loss, providing that log B vs 1/T is a straight line.

The latter relationship is the basis for the kinetic method used by Ozawa (Reference 25) and it does hold. Therefore, our kinetic treatment survives this complication.

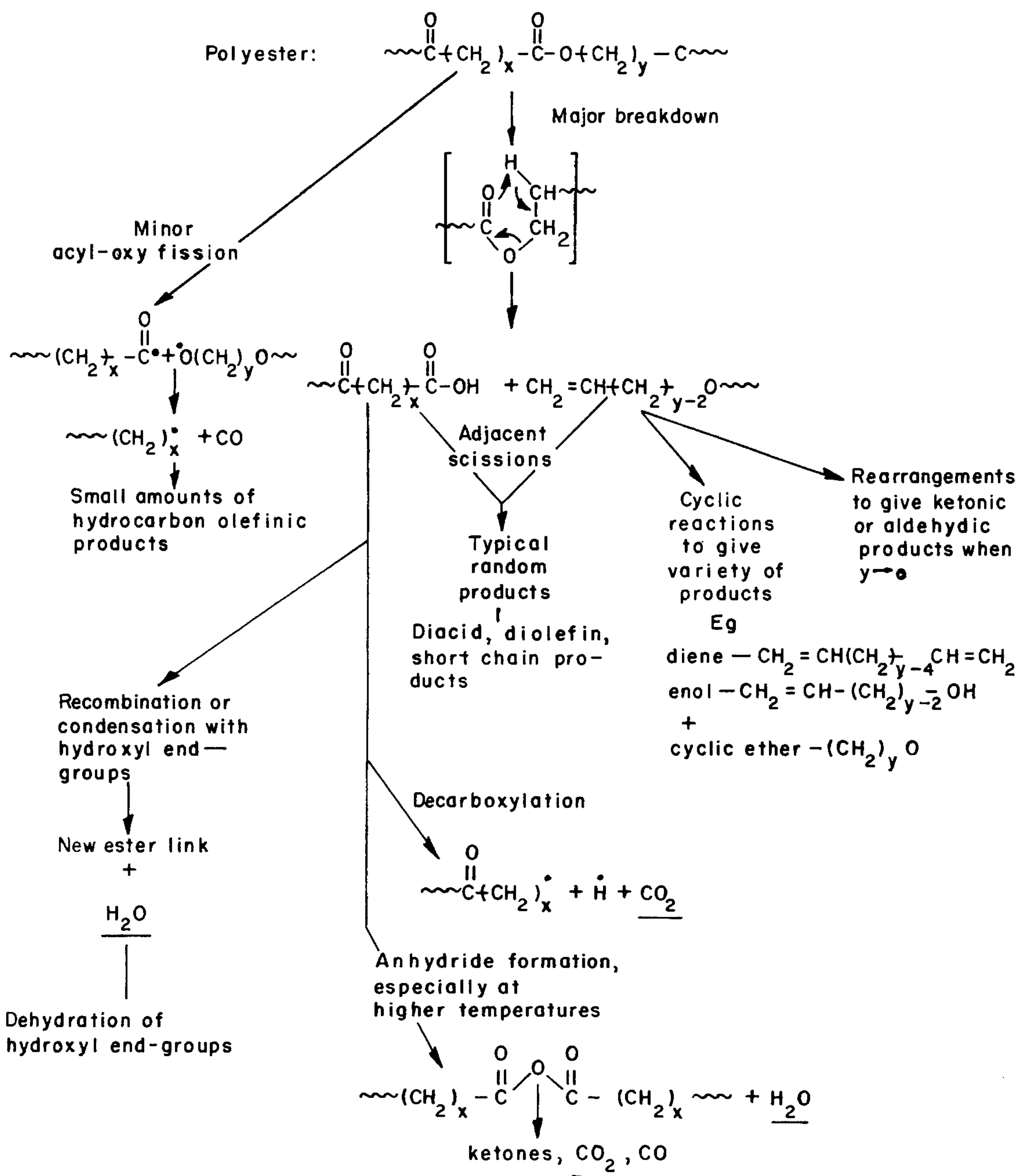
The random degradation discussion has so far been made in theoretical and mathematical terms. A more chemically descriptive look at this type of degradation can now be taken. Random degradation means essentially that degradation takes place at any position in the polymer chain and volatilization results from such scissions only (no pronounced unzipping as is observed in some vinyl polymers). During the initial stages of degradation, a polymer of high M.W. yields very little volatile material because, statistically, it is more probable that long chains give nonvolatile fragments. As the M.W. is rapidly reduced by scission, the probability, that the next scission will produce a volatile fragment increases, and a rate buildup is observed. The rate maximum, theoretically predicted to occur at 26% conversion, corresponds to the point at which a balance is reached between chain scission, which increases the total number of molecules and volatilization, which removes molecules from the system. The total number of chain ends is at a maximum at this point. After the maximum is reached, the rate curve falls in a manner similar to a first-order curve. Since the degradation reaction does not necessarily produce a volatile fragment, it is obvious that studying bond scission by following M.W. changes would bring a better understanding of the degradation. The fraction of bonds broken could be measured, and meaningful kinetic parameters deduced.

The above theories of random degradation were developed for chain degradation schemes in vinyl polymers but are based on the simpler case of stepwise random degradation observed for the pyrolysis of cellulosics and similar materials (Reference 26). It is considered likely that, primarily, polyesters degrade in this latter fashion since chain reactions and depolymerization are less easily conceived in a condensation polymer. There is also evidence that these polyesters show considerable deviations from the ideal random case. Although here the products of degradation consist of a spectrum of oligomeric species, as would be expected from random degradation, the weight loss consists

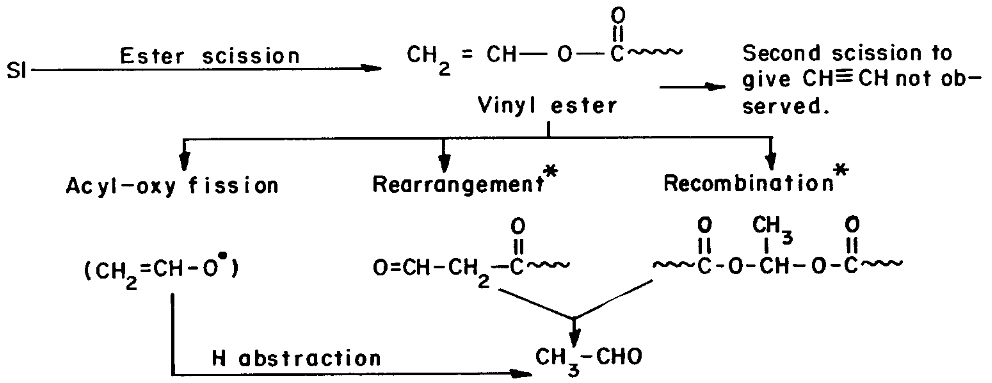
of significant amounts of small M.W. volatiles which would not be expected from pure random scission. In some polymers, e.g., S1, this volatile fraction is about as large as the heavy fraction. These low M.W. products arise from reactions subsequent to the random scission and introduce a nonrandom component to the overall reaction. The overall random picture is maintained, however, because the secondary reaction is particular to the end-groups produced by random scission and the rate of such reactions will reach a maximum corresponding to the situation where the concentration of end-groups is highest. A more puzzling feature is the absence of M.W. data to confirm the random mechanism. M.W. characteristics are generally very diagnostic of random scission. For the polyesters, the initially low degrees of polymerization would make any fall in M.W. less dramatic and would reduce the discrepancy between the initial and maximum rates, but a drop in M.W. would still be observed. In practice, no drop in M.W. could be observed and a cross-linking reaction, possibly arising from secondary free-radical reactions, was suspected. Ester interchange reactions (Reference 27) would also tend to maintain the M.W. but this would not produce insoluble material. It is difficult to predict what the effect of cross-linking should be on the kinetics of degradation. It would depend on the type and degree of cross-linking and on whether the cross-linking took place prior to degradation or during the degradation. The critical factor is whether the concentration of end-groups in the system is changed and whether classical M.W. correlations are applicable. In Reference 28, a linear polymer and a cross-linked sample derived from the former gave identical rates since the number of chain ends was not altered. Since the position of the maxima in the polyesters is unchanged, it would appear that the chain-end conversion characteristics are not altered by the cross-linking process. It is felt intuitively, however, that chain ends must be involved in the cross-linking process. Both olefinic and free-radical groups could take part in such processes although other reactions may also occur. The chain cross-links would be chains themselves and would be broken down by the same ester scission as the normal chain. Thus, in a loose network of this type, degradation can still go to completion without residue formation. The retention of the random kinetic features may simply result from the fact that the cross-link density is not high enough to significantly disturb the scission processes and the buildup of chain ends. The probable exception of S1 is discussed further in Section V.

REACTION MECHANISMS

It is concluded from MTA results that the overall degradation does not change noticeably over the temperature range studied; all of the intensity-vs-temperature curves for the numerous M/e values were similar both in shape and location. This suggests that a single basic mechanism applies and that no new mechanisms become available at higher temperatures. In analogy to the findings for poly(ethylene terephthalate), References 9 and 10, it is postulated that scission of the ester group to olefin and carboxylic acid groups is the primary degradation reaction. The cyclic concerted mechanism is upheld by the low temperature at which it occurs and the low E_a involved. Probably most of the volatile products are derived from secondary breakdown of the end-groups created by ester scission. The secondary reactions are fast enough to allow formation of small volatile products before a neighboring ester scission permits a chain fragment typical of a random degradation to distill out of the system. Some general reactions are formulated below.

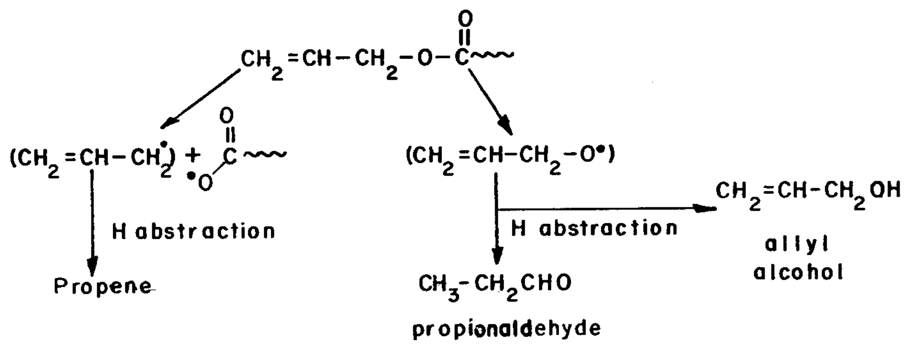

Polyester:
Major breakdown
Minor
acyl-oxy fission
+CO
Small amounts of
hydrocarbon olefinic
products
Adjacent
scissions
Typical
random
products
Diacid, diolefin,
short chain pro-
ducts
Cyclic
reactions
to give
variety of
products
Eg
diene
enol
+
cyclic ether
Rearrangements
to give ketonic
or aldehydic
products when
Recombination or
condensation with
hydroxyl end—
groups
New ester link
+
Dehydration of
hydroxyl end-groups
Decarboxylation
Anhydride formation,
especially at
higher temperatures
ketones, CO2, CO

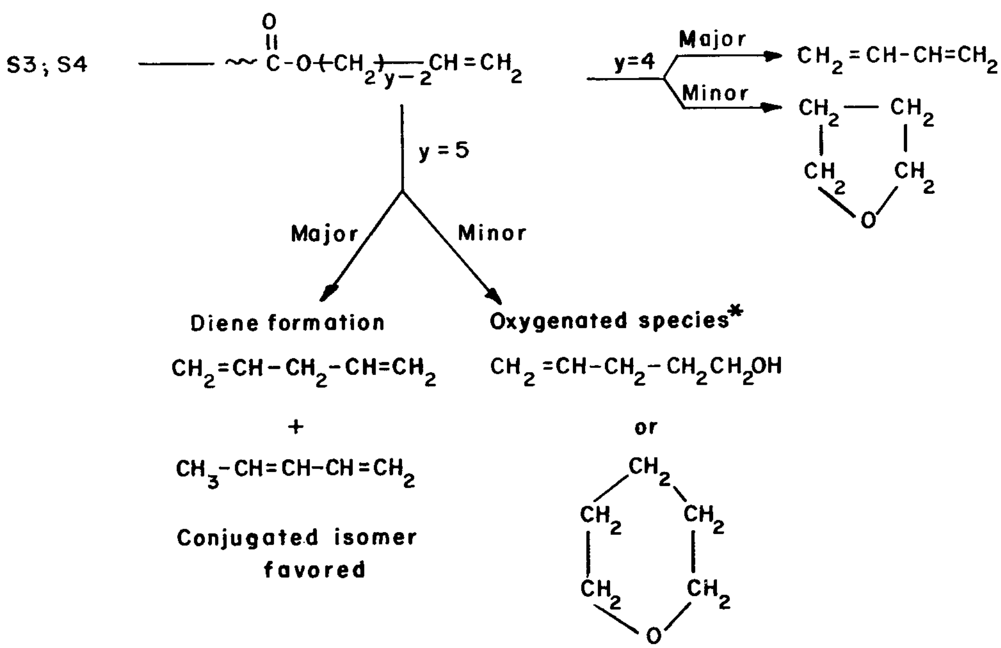
Within the general scheme, some specific reactions are found for the individual polymers:



*Observed in References 9 and 10.

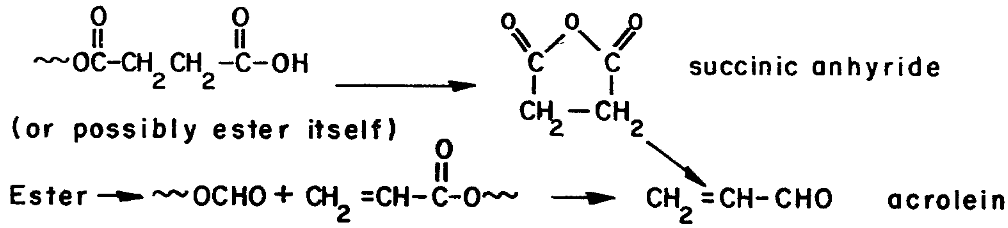
S2 —— Corresponding allylic ester undergoes several competitive modes of breakdown.





* Enol isomer concluded from GC/MS analysis but tetrahydropyran suggested by significant parent and p-1 peaks in the MTA spectrum.

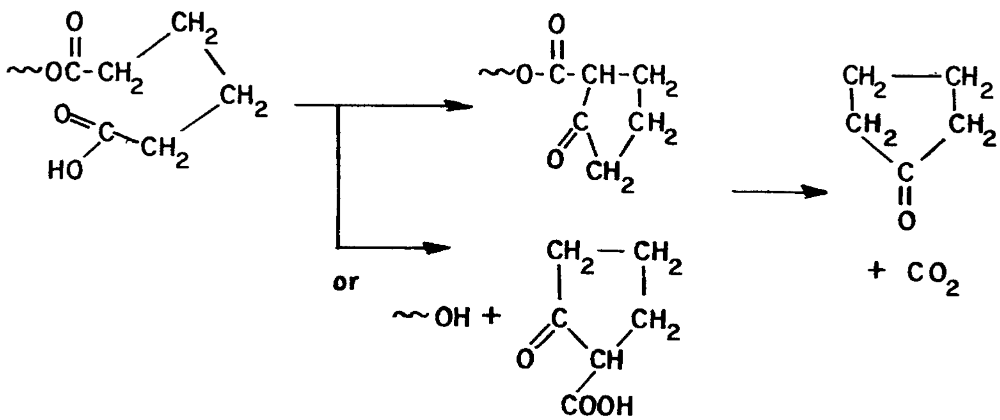
In the O series, reactions dependent on short acid-chain length are observed.

O1 

Acid breakdown may be competitive with ester scission

O2 Both anhydride and cyclic ketone formation

O3,O4 Cyclic ketone formation, e.g:



RELATIVE STABILITIES

Farre-Rius (Reference 12) has observed that the stability of polyesters increases if either the acid or diol chain length is increased, and that the rate increases as the number of ester links per standard weight of polymer increases. When total weight loss is being measured, however, this effect should diminish because higher homologs can lose more weight per act of scission. The present study clearly shows that the situation is not as simple as this; thus, polymers O1 and S1 have the same empirical formula, the same concentration of ester groups, but different rate curves (Figure 2) and different types of reaction mechanisms. Thus, the availability of specific secondary reactions to some polymers and not to others, and the varying relative importance of such secondary breakdowns to the overall random mechanism, can effectively mask any chain-length effect and cause anomalies from behavior predicted on a chain-length basis.

Initial stabilities can be examined by comparing initial TGA rates (Figure 9); supplementary information is also obtained from low-temperature isothermal studies (Table IV). Comparisons should be made with caution since other factors such as differences in initial M.W. would be expected to contribute to variations in initial rates. Correlations between rates and chain length are difficult to make and they depend on the temperature being used. Significant observations include the greater stability of S1 and the initial instability of O1 and O2. It is possible that O1 and O2 degrade at first by decomposition of the acid part, e.g., splitting out of anhydride, which is eventually superceded by the normal ester decomposition.

The apparently greater stability of S1 was also observed in the overall rate curves (Figure 2). S1 showed a further unusual feature, that of a high proportion of volatiles to condensates, almost 50/50. It is reasoned, therefore, that the reactive vinyl end-groups formed by ester scission cross-link at low temperatures but rearrange and decompose to acetaldehyde at higher temperatures. The effect of this is an initial inhibition of volatilization and a reduction in its total amount. It also affects the kinetics by distorting the random nature of the degradation to something intermediate between random and pseudo-first-order kinetics. Thus, in Figure 6, the maximum for S1 is pushed toward the origin. Since a first-order mechanism gives a more diffuse TGA rate curve than a random mechanism (Reference 18), the shape of the rate curve of S1 compared to the others confirms this conclusion. From the position of the rate curve, S1 must also have a higher E_a (or lower A) than the other polymers. Due to experimental errors, this could not be confirmed by the kinetic analysis performed. It is again reasoned that the degradation of S2 is intermediate between that of S1 and that of the other polymers.

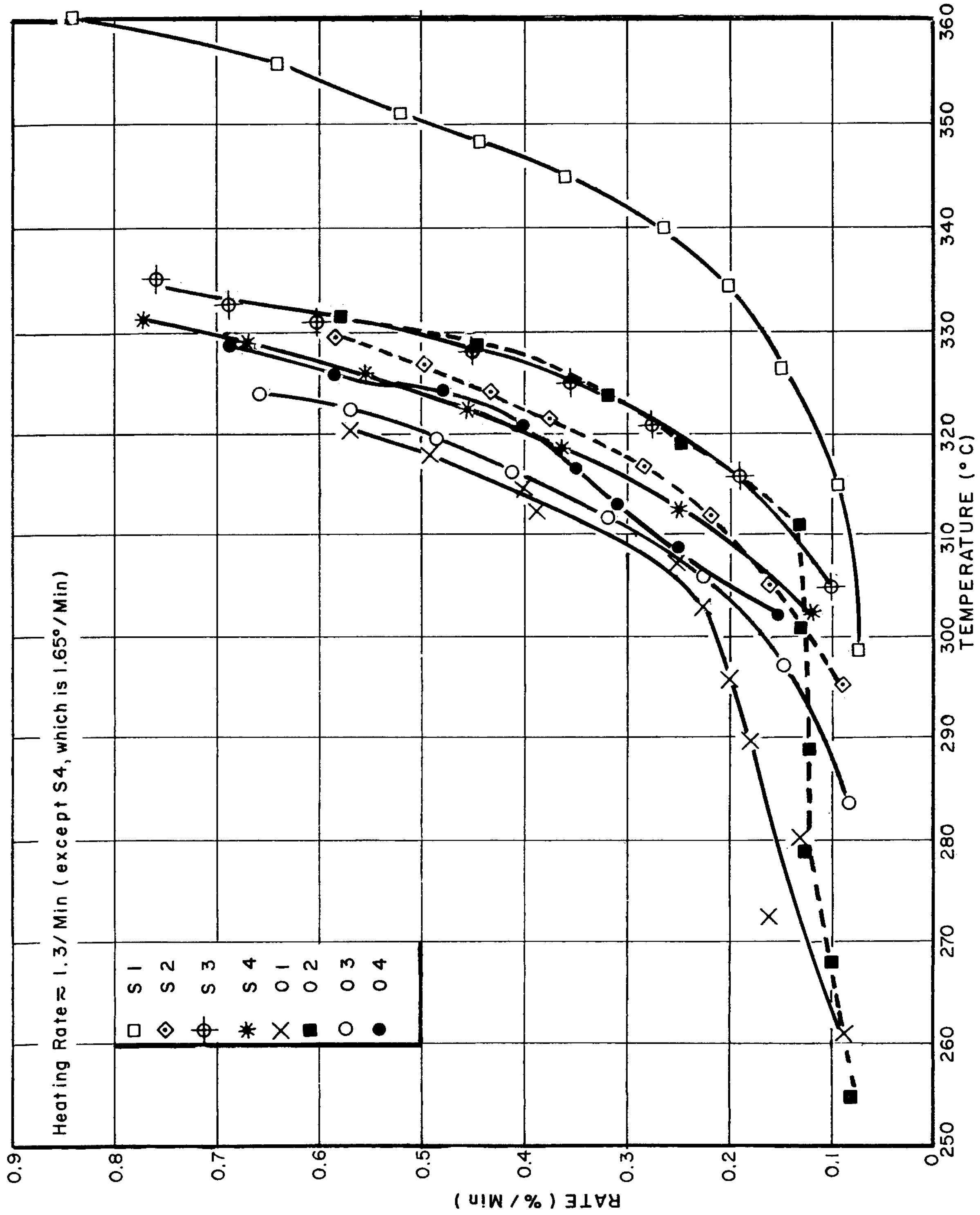


Figure 9. Degradation Rates for Early Stages of Weight Loss for Polyesters

SECTION VI

CONCLUSION

The overall degradations of eight polyesters suggest that a similar basic degradation applies and that differences arise from secondary reactions of end-groups formed by ester scission. Most of the polymers studied follow approximately a random mechanism although numerous deviations from the classical view of random kinetics are observed. The first-order kinetics concluded by Farre-Rius and Guiochon (Reference 12) does not contradict the present findings since a close study of their data shows that the rate curves undergo a maximum, and this is incompatible with first-order kinetics. Only if cross linking becomes important or if the initial M.W. approaches the critical evaporation size, can the kinetics tend toward the first-order case. Appreciable amounts of small volatile products arise from secondary breakdown of end-groups so that larger volatile fractions are observed than would be expected from a simple random mechanism. Most products can be explained without recourse to competitive ester decompositions (Reference 12) and it is concluded that the cyclic concerted decomposition observed in simple esters is the important first step in polyester pyrolysis. The observed kinetic parameters, $E_a \simeq 40$ kcal mole^{-1} and $A \simeq 10^{12}$ min^{-1}, are lower than those observed for simple ester pyrolysis, but this is hardly surprising in view of the greater complexity of polyester degradation and the secondary breakdowns which contribute to overall activation energies.

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13. ABSTRACT

A study has been made of the pyrolysis of eight aliphatic polyesters prepared from various diacids and diols. The polymers start to degrade about 275°C by random scission of the ester linkage and are comparable to poly(ethylene terephthalate) with respect to thermal stability. Providing a β-hydrogen atom is available in the diol portion of the ester, which was the case for the polymers studied, the classical cyclic mechanism observed for the decomposition of simple esters is applicable. Differences in degradation behavior are best explained in terms of secondary reactions which are dependent upon the nature of the end groups formed by scission and on the chain length of the acid and diol used to prepare the polymer. Thus, olefinic end groups break down to aldehydes, dienes, cyclic ethers and enols while acid end groups give carbon dioxide, cyclic ketones (C_5-C_7 diacids) and cyclic anhydrides (C_4, C_5 diacids). Water is produced by anhydride formation and dehydration of hydroxyl end groups.

The overall kinetics were consistent with a random mechanism but deviations from the simple random picture were concluded for some polymers and probably resulted from cross linking. Kinetic parameters were evaluated from programmed TGA data; activation energies of approximately 40 kcal./mole and preexponential factors of about 10^{12} min^{-1} were obtained.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Degradation Polyesters Polymers Thermal						